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Tris(pyrazolyl)phosphine Oxide and Tris(triazolyl)phosphine Oxide Scorpion Ligands

DFT calculations were performed on copper(I) complexes of neutral scorpion ligands based on either pyrazolyl (Pz) or triazolyl (Tz) rings with both methane and phosphine oxide apices, that is, HC(Pz)₃, OP(Pz)₃, HC(Tz)₃, and OP(Tz)₃. The analyses reveal that all four ligands have similar donor properties and that their differences are easily compensated by the proper choice of substituents. This computational study strongly suggests that the readily synthesizable neutral phosphine oxide capped scorpion ligands should have broad applicability. Experimentally, the two OP-capped ligands act differently on copper(I) complexation. With OP(Tz)₃ a crystallographically characterized dimeric tris(triazolyl)-phosphine oxide based copper(I) complex was obtained, whereas instead a monomer has been reported for OP(Pz)₃.

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3.1 Introduction

Scorpion ligands are among the most versatile ligands for transition metal coordination. Their complexes have found numerous applications in inorganic and organometallic chemistry. In particular, the tris(pyrazolyl)borates (scorpionates, $\text{HB}(\text{Pz})_3$ (**A**), see Figure 3.1) with their anionic boron apex have been widely adopted, including in a large number of catalytic studies.^[1-3] In contrast, the corresponding neutral analogues with a carbon atom at the apex ($\text{HC}(\text{Pz})_3$ (**B**)) have received far less attention,^[4,5] likely owing to their limited accessibility. This is unfortunate, because of the demonstrated versatility and ability of their transition metal complexes to function as catalysts.^[6-8] In this study we explore alternatives.

We became interested in the neutral phosphine oxide analogues ($\text{OP}(\text{Pz})_3$ (**C**)) with a phosphorus atom at the apex. These ligands are readily synthesized in high yield from OPCl_3 and pyrazole in the presence of a base and form complexes with transition metals.^[9] For example, Cu(I) coordinates to each of the “free” nitrogen atoms of the three pyrazolyl groups with the fourth ligand being CO, triphenylphosphine or acetonitrile, for example, $[\text{C}^{\text{Me2}}\text{Cu}(\text{NCMe})][\text{PF}_6]$ (Figure 3.2, left). The group of Peterson was the first to report on the tris(pyrazolyl)phosphine oxides (**C**)^[10,11] and their coordination chemistry.^[12,13] This chemistry was subsequently extended,^[14-19] notably by Tolman and co-workers with chiral ligands based on chiral pyrazoles.^[15-18]

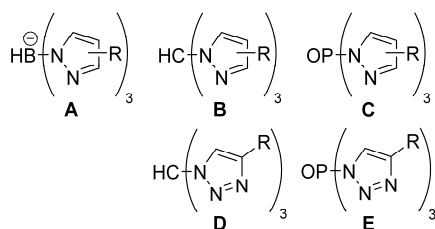


Figure 3.1. Scorpion-type ligands.

Recently, we showed that the related tris(triazolyl)phosphine oxides (OP(Tz)₃ (**E**)) coordinate to transition metals and reported the molecular structure of the RhCl₃ complex E^{Ph}RhCl₃ (Figure 3.2, right).^[20] These neutral ligands **E** are readily accessible by a triple Click-reaction, that is, a copper catalyzed azide–alkyne cyclization, of an azide with tris(alkynyl)phosphine oxide. The corresponding phosphines can be obtained by reduction of the phosphine oxide.^[20] Bräse and co-workers subsequently reported a one-pot modification by treating alkynylmagnesium bromides with azides followed by addition of PCl₃. The resulting ligands were suitable for Zn complexation.^[21] Templeton's group found the performance of hemilabile tris(triazolyl)phosphine oxides in Pt-mediated C–C and C–H bond formations under mild reaction conditions to be superior to those of the tris(pyrazolyl)-based ligands **A** and **B**.^[22,23] These recent developments bode well for advancing the OP(Tz)₃ ligand **E** in homogeneous catalysis. It is then surprising that, to the best of our knowledge, no information is available on the functioning of the corresponding carbon analogue HC(Tz)₃ (**D**).

In this study we set out to examine computationally the differences between the ligand properties of the carbon and phosphorus analogues of (1) the tris(pyrazolyl)-based systems **B** and **C** and of (2) the tris(triazolyl)-based systems **D** and **E**. We further focus on the features of the PO-containing ligands **C** and **E**, which is driven by their simple synthetic access and the convenient in situ monitoring of their integrity by ³¹P NMR spectroscopy. To demonstrate the validity of our computational findings, we also report on the synthesis of the first Cu complex of OP(Tz)₃ (**E**). The dimeric nature of this complex reveals extra functionality of ligand **E**.

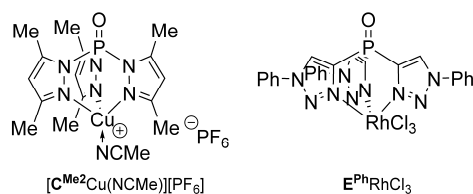


Figure 3.2. Typical OP(Pz)₃ and OP(Tz)₃ complexes.

3.2 Results and Discussion

3.2.1 Calculated Geometries of the Free Ligands

We started the DFT calculations at the BVP86/6-311G(d,p) (SDD for Cu) level of theory^[24-29] by full geometry optimization of the four parent ligands **B–E** (Figure 3.1, R = H). The results are shown in Figure 3.3. The geometry of carbon ligand HC(Pz)₃ (**B**), and also of the phosphorus ligand OP(Pz)₃ (**C**; Figure 3.3, top), is similar to that found in the crystal structure of the phenyl derivative HC(Pz^{Ph})₃.^[30] They show that the unsubstituted nitrogen atom of two of the pyrazolyl rings is orientated toward the apex, whereas that of the third ring is directed away from the apex. The geometries of the corresponding triazole-containing carbon and phosphorus ligands HC(Tz)₃ (**D**) and OP(Tz)₃ (**E**) have instead near C₃-symmetrical geometries as shown

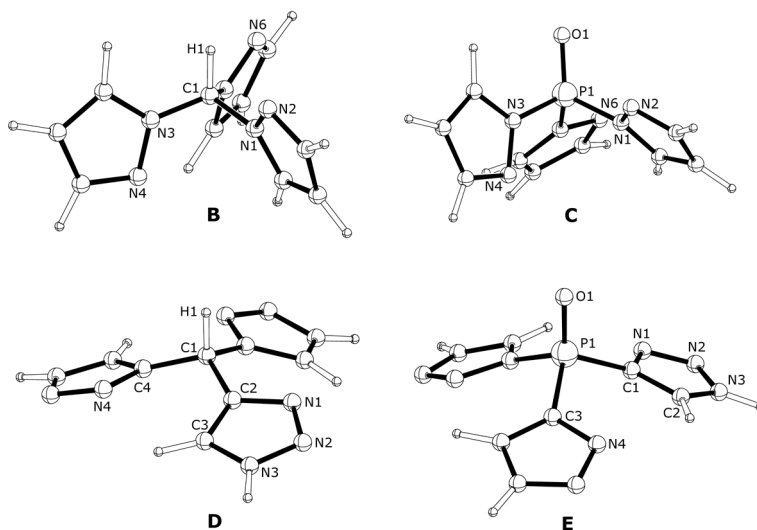


Figure 3.3. Computed structures for the parent ligands **B–E**. Selected bond lengths (Å) and angles (°), **B**: C1–N1 = 1.456, C1–N3 = 1.457, C1–H1 = 1.096, N1–N2 = 1.363; N1–C1–N3 112.1. **C**: P1–N1 = 1.717, P1–N3 = 1.721, P1–O1 = 1.480, N1–N2 = 1.378; N1–P1–N3 104.2. **D**: C1–C2 = 1.520, C1–C4 = 1.520, C1–H1 = 1.110, C2–C3 1.387, C2–N1 1.375, N1–N2 = 1.313, N2–N3 = 1.356, N3–C3 1.360; C2–C1–C4 112.9. **E**: P1–C1 = 1.821, P1–C3 = 1.822, P1–O1 = 1.505, C1–C2 1.389, C1–N1 1.380, N1–N2 = 1.308, N2–N3 = 1.364, N3–C2 1.356; C1–P1–C3 103.5.

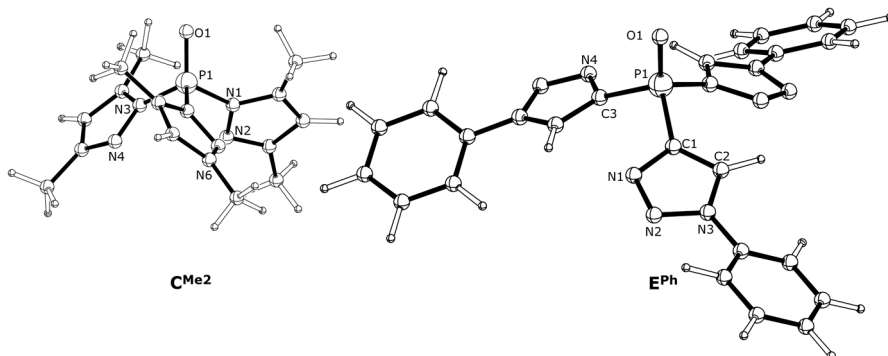


Figure 3.4. Computed structures for the substituted ligands **CMe₂** and **E^{Ph}**. Selected bond lengths (Å) and angles (°), **CMe₂**: P1-N1 = 1.714, P1-N3 = 1.715, P1-O1 = 1.491, N1-N2 = 1.386; N1-P1-N3 104.3. **E^{Ph}**: P1-C1 = 1.823, P1-C3 = 1.822, P1-O1 = 1.505, C1-C2 1.387, C1-N1 1.378, N1-N2 = 1.305, N2-N3 = 1.377, N3-C2 1.362; C1-P1-C3 103.4.

in Figure 3.3 (bottom). Jointly, the rings have a “flat” orientation with the triazole N atoms in the position of N1 pointing toward the neighboring ring albeit that they are slightly tilted toward the apex for the carbon-centered ligand **D**.

Because of the known influence of substituents on the scorpionate ligands,^[1-3] we examined their effect on the phosphorus centered ligands **C** and **E**, respectively, by 3,5-dimethyl substitution on the pyrazole rings (**CMe₂**) and by introducing 1-phenyl groups on the triazole rings (**E^{Ph}**). Their fully optimized geometries are shown in Figure 3.4. Both ligand systems and some transition metal complexes thereof are experimentally known, such as those shown in Figure 3.2.^[9,20] The geometry of the lowest-energy form of the **CMe₂** ligand is nearly *C*₃ symmetric. Evidently, introduction of the methyl groups causes a “ring flip” of two of the pyrazolyl rings of **C**. Introduction of the phenyl substituent on the triazole rings (**E^{Ph}**) has little effect on the geometry of **E**, which is hardly surprising as the phenyl substituents are positioned far from both the PO apex and the other rings.

3.2.2 Copper(I) Complexes

Next, we computationally examined the complexation of the ligands using the Cu(NCMe)₄ cation that yields acetonitrile coordinated copper complexes **1B–E**

(Table 3.1). Because of their inherent limited flexibility, the complexes were calculated within C_3 or C_{3v} symmetry. The formation of the Cu–NCMe complexes of both HC- and OP-centered parent pyrazolyl based ligands **B** and **C** have very modest exothermicities of merely 0.3 and 1.6 kcal/mol, respectively (see Table 3.1), which is probably caused by the needed “ring flip” of two pyrazole rings. This presumption is supported by the Cu–NCMe complexation energies of the parent HC and OP centered triazolyl based ligands **D** and **E**, which show larger exothermicities of 5.2 and 5.9 kcal/mol, respectively. Substitution, be it methyl groups on the pyrazole rings or a phenyl on the triazole ring, enhances the exothermicity of complexation. Thus, the reaction energies for the OP centered **C^{Me2}** and **E^{Ph}** ligands amount to –10.1 and –10.0 kcal/mol, respectively. These larger binding energies may reflect the more readily achieved coordination mode of the ligand as well as enhanced N–Cu interactions. It then also appears that both ligands are equally good for forming the desired organometallic complexes.

To obtain insight into the donor ability of the neutral OP-based scorpion ligands, we studied the carbon monoxide complexes **2B–E** (Table 3.1). Namely, the strength of the ν (CO) stretching frequency provides insight into the electron density of the metal atom and thus indirectly into the electron-donor ability of the scorpion ligand.

Table 3.1. Calculated Gibbs free energies for the reactions of scorpion type ligands and their monomeric copper complexes **1L** and **2L** including computed carbonyl stretching frequencies.

$L \xrightarrow[-3N\equiv CMe]{+[Cu(N\equiv CMe)_4]^+} [LCu(C\equiv CMe)]^+ \xrightarrow[-N\equiv CMe]{+C\equiv O} [LCu(C\equiv O)]^+$				
		1L		2L
	L	ΔG (kcal/mol)	ΔG (kcal/mol)	ν (CO) (cm ⁻¹)
B	HC(Pz) ₃	–0.3	–0.4	2132
C	OP(Pz) ₃	–1.6	0.7	2132
D	HC(Tz) ₃	–5.2	0.9	2135
E	OP(Tz) ₃	–5.9	1.0	2139
C^{Me2}	OP(PzMe ₂) ₃	–10.1	–0.5	2108
E^{Ph}	OP(TzPh) ₃	–10.0	–1.5	2127

The geometries of all complexes were optimized with C_{3v} symmetry (Figure 3.5). These complexes are virtually (within 1.0 kcal/mol) isoenergetic with the acetonitrile complexes (Table 3.1). The calculated CO stretching frequency of the two parent HC- and OP-based pyrazolyl complexes **2B** and **2C** were found to be identical (2132 cm^{-1}) and very similar to the two corresponding triazolyl based complexes **2D** (2135 cm^{-1}) and **2E** (2139 cm^{-1}). This suggests that the four scorpion ligands, whether they have HC or OP apices and contain pyrazolyl or triazolyl rings, have similar donor

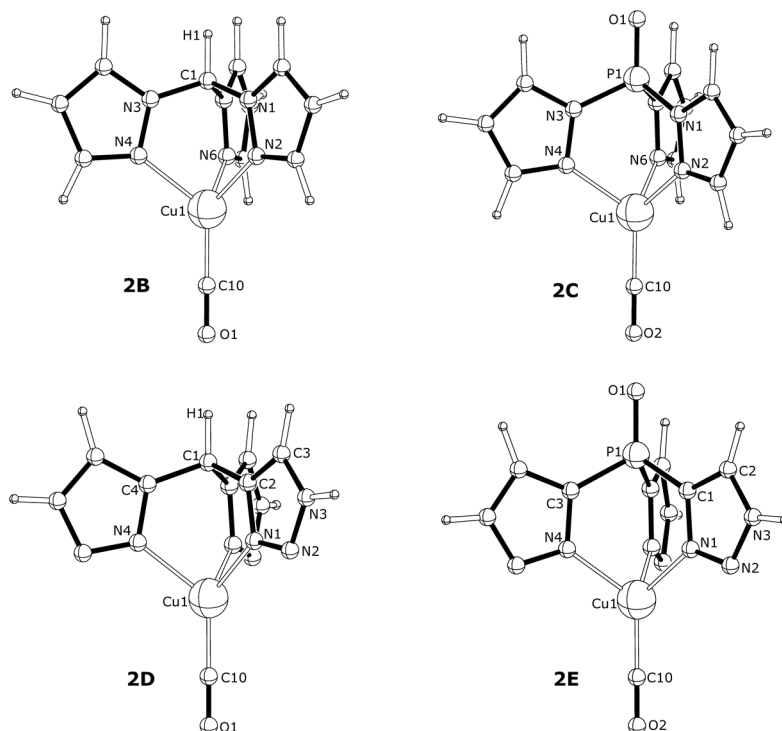


Figure 3.5. Computed structures for **2B–E**. Selected bond lengths (Å) and angles (°) for **2B**: C1–N1 = 1.458, C1–H1 = 1.096, N1–N2 = 1.365, Cu1–N2 2.096, Cu1–C10 1.804, C10–O1 1.146; N1–C1–N3 111.2, N4–Cu1–N2 87.6; **2C**: P1–N1 = 1.722, P1–O1 = 1.475, N1–N2 = 1.383, Cu1–N2 2.093, Cu1–C10 1.813, C10–O2 1.145; N1–P1–N3 103.6, N4–Cu1–N2 91.3; **2D**: C1–C2 = 1.517, C1–H1 = 1.099, C2–C3 1.382, C2–N1 1.373, N1–N2 = 1.315, N2–N3 = 1.344, N3–C3 1.364, Cu1–N1 2.101, Cu1–C10 1.810, C10–O1 1.145; C2–C1–C4 109.4, N4–Cu1–N1 86.6; **2E**: P1–C1 = 1.823, P1–O1 = 1.495, C1–C2 1.384, C1–N1 1.378, N1–N2 = 1.313, N2–N3 = 1.348, N3–C2 1.360, Cu1–N1 2.100, Cu1–C10 1.820, C10–O2 1.144; C1–P1–C3 101.2, N4–Cu1–N1 90.4.

properties. It is noteworthy that the Cu–C bond lengths of the OP-based ligands **2C** and **2E** are approximately 0.01 Å longer than those of **2B** and **2D**, respectively, whereas the CO bond length is essentially the same for all (ca. 1.145 Å).

Substituting the OP-based ligands with methyl or phenyl groups as in OP(Pz^{Me2})₃ (**C^{Me2}**) and OP(Tz^{Ph})₃ (**E^{Ph}**) seems to change little (Figure 3.6). Replacing the acetonitrile ligand for a CO group becomes slightly exothermic by ≤ 1.5 kcal/mol, but the calculated CO stretching frequencies are smaller by 25 cm^{−1} for the pyrazolyl ligand and 12 cm^{−1} for the triazolyl ligand (Table 3.1). Presumably, the substituents contribute to an increase in electron density of the metal centers which results in a slightly increased π back-donation to CO.^[9]

3.2.3 Preparation of Copper Complexes of OP(Tz^{Ph})₃

The computational analysis suggests on the one hand that the OP-based scorpion ligands may be viable alternatives to the neutral HC-based ones and on the other that there is at best a modest distinction between the Cu(I)-complexation of the pyrazolyl and triazolyl based ligands **C^{Me2}** and **E^{Ph}**. Earlier, we reported already on the X-ray crystal structure of [C^{Me2}Cu(NCMe)][PF₆].^[9] Hence, we wondered if a similar complex could be prepared from **E^{Ph}**. To this end, OP(Tz^{Ph})₃ (**E^{Ph}**) and [Cu(NCMe)₄][PF₆] were treated in CH₂Cl₂ at room temperature for 3 h to render,

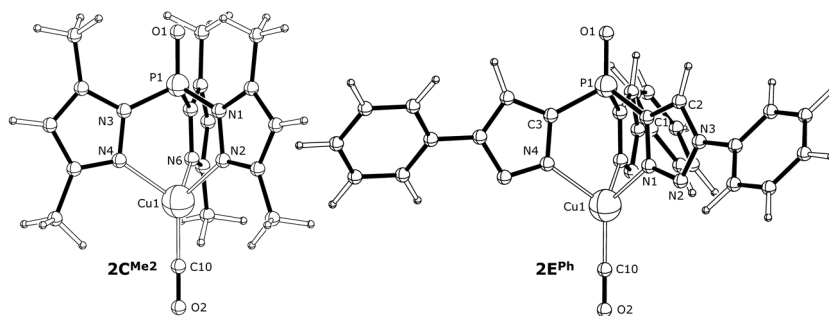
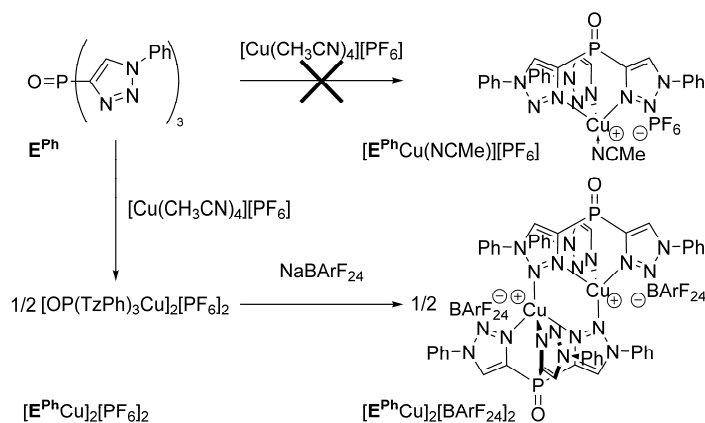


Figure 3.6. Computed structures for **2C^{Me2}** and **2E^{Ph}**. Selected bond lengths (Å) and angles (°), **2C^{Me2}**: P1–N1 = 1.723, P1–O1 = 1.479, N1–N2 = 1.392, Cu1–N2 2.079, Cu1–C10 1.808, C10–O2 1.148; N1–P1–N3 104.5, N4–Cu1–N2 91.7. **2E^{Ph}**: P1–C1 = 1.822, P1–O1 = 1.497, C1–C2 1.383, C1–N1 1.374, N1–N2 = 1.315, N2–N3 = 1.358, N3–C2 1.367, Cu1–N1 2.095, Cu1–C10 1.817, C10–O2 1.145; C1–P1–C3 101.3, N4–Cu1–N1 90.7.

after removal of all volatiles, a poorly soluble beige solid in 98% yield. Although both the ^1H and ^{31}P NMR spectra of this material showed hardly any significant shifts relative to the spectra of the ligand E^{Ph} , its ESI mass spectrum gave an m/z peak at 542.0634, suggestive of Cu^+ -complexation, but without an acetonitrile ligand that was also not observed in the ^1H NMR spectrum. Evidently, the anticipated $[\text{E}^{\text{Ph}}\text{Cu}(\text{NCMe})][\text{PF}_6]$ was not formed (Scheme 3.1). Attempts to obtain suitable crystals for X-ray analysis were unsuccessful.

We next tried to introduce a CO ligand by exposing a solution of the presumed tris(triazolyl)phosphine oxide Cu(I) complex in CH_2Cl_2 to a CO atmosphere in an analogous freeze–pump–thaw procedure that was used for the HC- and OP-based pyrazolyl ligands **B**^[31] and **C**.^[9] Whereas at ambient temperature the reaction mixture was a suspension under N_2 , thawing under CO gave a clear solution from which a precipitate resulted upon addition of pentane. This material did not show a CO frequency by IR spectroscopy in contrast to products obtained from the same procedure used for ligand **B** and **C**. We presume that the CO-ligation to the $[\text{E}^{\text{Ph}}\text{Cu}][\text{PF}_6]$ complex is relatively weak and that the labile carbonyl species formed loses its ligand once the CO pressure is released. Again, attempts to obtain crystals of the resulting material suitable for X-ray diffraction failed.

To enhance the solubility of the solid material, we exchanged the PF_6 anion for tetrakis((3,5-trifluoromethyl)phenyl)borate (BARF_{24}) by stirring a CH_2Cl_2 suspension



Scheme 3.1. Complexation of E^{Ph} .

with NaBArF₂₄.^[32,33] The resulting complex proved readily soluble in polar organic solvents, like THF and CH₂Cl₂. Crystals obtained from CH₂Cl₂/pentane mixture were suitable for an X-ray crystal structure determination, which revealed the dimeric structure [E^{Ph}Cu]₂[BArF₂₄]₂ (Figure 3.7). The asymmetric unit of the crystal structure contains two half molecules of the dimeric [E^{Ph}Cu] cation, two [BArF₂₄] anions, and one molecule of CH₂Cl₂.

The crystal structure of [E^{Ph}Cu]₂[BArF₂₄]₂ shows two copper centers with distorted tetrahedral coordination. Each copper atom is bound by a tridentate OP(Tz^{Ph})₃ ligand and a medial triazolyl nitrogen atom of the other ligand completes the coordination sphere. The two OP(Tz^{Ph})₃Cu fragments within a dimer are crystallographically related by an inversion center. The central (Cu–N–N)₂ hexagon is nearly flat, with the largest deviation from planarity being a dihedral angle of –14.31°. The Cu...Cu distance of 3.7898(8) Å does not suggest any direct bonding interaction of the metal atoms.^[34–36] The OP(Tz^{Ph})₃ ligand shows similar features as found in the two crystallographically characterized examples known so far, that is, the RhCl₃^[20] and PtMe₃[BArF₂₄]^[23] complexes of E^{Ph}. The bond lengths of the proximal triazolyl nitrogen atoms to the copper atom are 2.080(2), 2.113(2) and 2.165(2) Å. They all fall within the range of distances reported in the literature for complexes with Cu(I)-triazolyl bonds. Among these complexes, only two display triazolyl rings bridging two Cu centers.^[34,35] In particular, the Cu dimer complex containing two tris(triazolylmethyl)amine ligands that was reported by Donnelly *et al.*^[34] shows significant resemblance to [E^{Ph}Cu]₂[BArF₂₄]₂, except for the shorter bridging N–Cu bond of 1.979(2) Å in [E^{Ph}Cu]₂[BArF₂₄]₂ (compare with 2.038(2) Å in the literature^[34]). It was shown that this tris(triazolylmethyl)amine-copper dimer is an excellent catalyst for the azide–alkyne cycloaddition.^[34] The active species presumably is the corresponding monomer, which suggests facile dissociation of the dimer under catalytic conditions. This holds great promise for [E^{Ph}Cu]₂[BArF₂₄]₂ as a catalyst precursor.

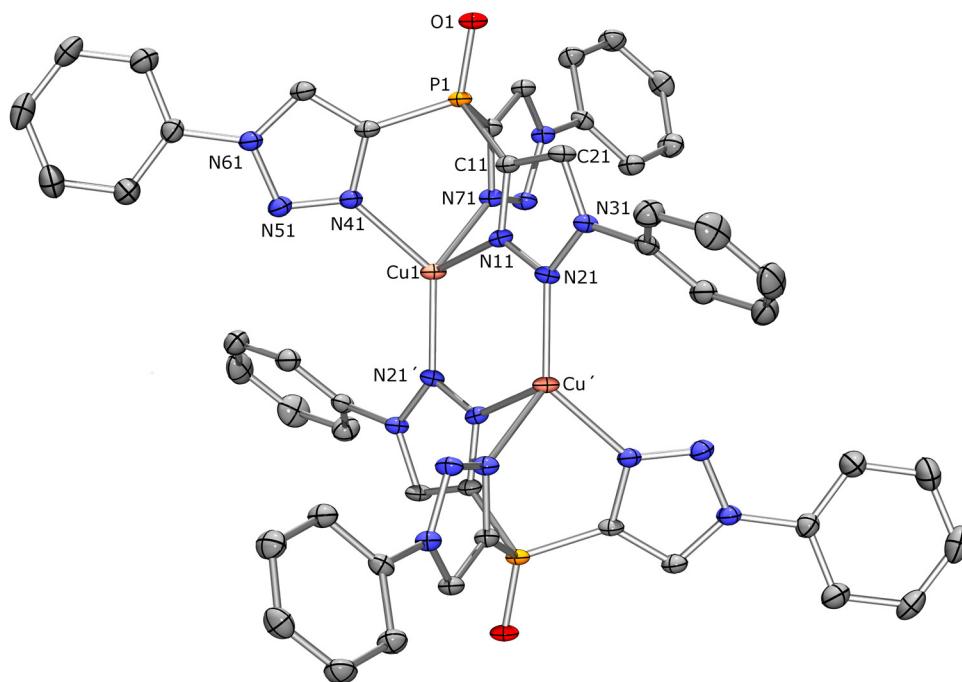


Figure 3.7. Displacement ellipsoid plot of $[\text{E}^{\text{Ph}}\text{Cu}]_2[\text{BArF}_{24}]_2$ drawn at the 50% probability level. Only one of two independent cationic dimers is displayed. $[\text{BArF}_{24}]$ anions, all hydrogen atoms, and the CH_2Cl_2 solvent molecule are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{CuI-N11} = 2.165(2)$, $\text{CuI-N21}' = 1.979(2)$, $\text{PI-O1} = 1.4688(19)$, $\text{PI-C11} = 1.805(3)$, $\text{N11-C11} = 1.358(3)$, $\text{N11-N21} = 1.314(3)$; $\text{O1-PI-CuI} = 177.52(11)$, $\text{N11-CuI-N41} = 92.56(9)$, $\text{CuI-N11-N21} = 132.00(17)$, $\text{O1-PI-C11} = 115.66(12)$, $\text{C11-PI-C91} = 104.60(13)$. Symmetry code: (i) $-x, 1-y, 1-z$.

3.3 Conclusion

The calculated Gibbs free energy for the complexation reaction of the monomeric model of both the OP- and HC-capped scorpion ligands shows that the main difference between the ligands is due to their different five membered rings. Namely, the $\text{OP}(\text{Tz})_3$ ligand releases 4–5 kcal/mol more than the $\text{OP}(\text{Pz})_3$ ligand and the same holds for the HC centered analogues. The differences in complexation energy upon change of the apex are rather subtle (within 1.5 kcal/mol). When introducing real substituents in the OP centered systems, the energy differences for

the reactions considered are within 1 kcal/mol, thereby stressing the similarity of the primary coordination site of these ligand types. This illustrates that the OP(Tz)₃ (**E**) and OP(Pz)₃ (**C**) ligands offer easily accessible metal supporting platforms that can be decorated at will to steer their steric and electronic (for **C**) or solely electronic (for **E**) properties. Such effects are well established for the anionic tris(pyrazolyl)borates **A** and the current ligand systems offer the opportunity to extend this chemistry to neutral ligands.

Both OP-centered scorpion ligands investigated in this study can support the Cu(I) cation, which allows a direct comparison of their ligand properties. The experimentally observed difference is the ability of the OP(Tz^{Ph})₃ ligand to form a dimer, thereby eliminating the need for additional ligands. This extra feature of the OP(Tz)₃ ligand makes it even more interesting to develop its chemistry further.

3.4 Experimental Section

Computations

All density functional theory calculations (BVP86)^[24-26] were performed with the Gaussian09 suite of programs,^[37] using the SDD basis set and pseudopotentials for copper^[27] and the 6-311G(d,p) basis set^[28,29] for all other atoms. Each structure was confirmed to be a ground state by frequency calculations.

General Procedures.

All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques: CH₂Cl₂ was distilled from CaH₂, and THF, Et₂O and DME from sodium wire. Tris(1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphine oxide (**E^{Ph}**),^[20] tetrakis(acetonitrile)copper(I) hexafluorophosphate^[38] and NaBarF₂₄^[32,33] were prepared according to literature procedures. NMR spectra were recorded with a Bruker Avance 250, a Bruker Avance 400 or on a Bruker Ultrashield 500 spectrometer at 298 K. ¹H and ¹³C NMR spectra were referenced internally to residual solvent resonances (CD₃CN: ¹H: δ = 1.94 ppm (CD₂HCN), ¹³C{¹H}: δ = 1.32 ppm; CD₂Cl₂: ¹H: δ = 5.32 ppm (CDHCl₂), ¹³C{¹H}: δ = 53.84 ppm). Other nuclei were referenced to external standards: ¹⁹F: BF₃·Et₂O (δ = 0.0 ppm) and ³¹P: 85% H₃PO₄ (δ = 0.0 ppm). IR spectra were recorded with a Shimadzu FTIR-8400S

spectrophotometer, using the ATR technique. Peak intensities are marked as follows: s = strong, m = medium, w = weak. High resolution electrospray ionization-mass spectrometry (HR ESI-MS) was performed using a Bruker MicroTOFQ, with ESI in positive mode (capillary voltage 4.5 kV). Melting points were measured on samples in unsealed capillaries with a Stuart Scientific SMP3 melting point apparatus.

Complexations

Preparation of $[\text{OP}(\text{C}_2\text{HN}_3\text{Ph})_3\text{Cu}]_2[\text{PF}_6]_2$ ($[\text{E}^{\text{Ph}}\text{Cu}]_2[\text{PF}_6]_2$) $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ (99 mg, 0.266 mmol) was added to a solution of $\text{E}^{\text{Ph}}\cdot 0.325\text{CH}_2\text{Cl}_2$ (130 mg, 0.266 mmol) in CH_2Cl_2 (5 mL). After 2 h 15 min of stirring, all volatiles were removed under reduced pressure, and $[\text{E}^{\text{Ph}}\text{Cu}]_2[\text{PF}_6]_2$ was obtained as a yellow solid in 98% yield (0.19 g, 0.26 mmol). M.p. 174–184 °C (decomposition without melting). ^1H NMR (500 MHz, CD_3CN): δ 7.53 (t, 3H, $^3J_{\text{HH}} = 7.5$ Hz, H_{para}), 7.60 (t, 6H, $^3J_{\text{HH}} = 7.4$ Hz, H_{meta}), 7.86 (d, 6H, $^3J_{\text{HH}} = 7.4$ Hz, H_{ortho}), 8.87 (s, 3H, $\text{P}-\text{C}=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_3CN): 122.2 (s, C_{ortho}), 130.6 (s, C_{meta}), 130.9 (s, C_{para}), 131.0 (d, $^2J_{\text{CP}} = 29.3$ Hz, $\text{P}-\text{C}=\text{CH}$), 137.5 (s, C_{ipso}), 142.2 (d, $^1J_{\text{CP}} = 155.1$ Hz, $\text{P}-\text{C}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CD_2Cl_2): δ -141.2 (septet, 1P, $^1J_{\text{PF}} = 706.2$ Hz, PF_6), -5.2 (s, 1P, PO). $^{19}\text{F}\{^1\text{H}\}$ NMR (235.4 MHz, CD_2Cl_2): δ -69.6 (d, $^1J_{\text{FP}} = 706.3$ Hz). IR: ν 1506 (m), 1234 (w), 1177 (w), 1066 (w), 993 (w), 821 (s), 760 (s), 691 (s), 580 (s), 561 (s). HR ESI-MS: calcd for $\text{C}_{24}\text{H}_{18}\text{CuN}_9\text{OP}$ ($\text{M} - \text{PF}_6 - \text{CH}_3\text{CN}$): 542.0662, found: 542.0634.

Preparation of $[\text{OP}(\text{C}_2\text{HN}_3\text{Ph})_3\text{Cu}]_2[\text{BArF}_{24}]_2$ ($[\text{E}^{\text{Ph}}\text{Cu}]_2[\text{BArF}_{24}]_2$) A suspension of $[\text{OP}(\text{C}_2\text{HN}_3\text{Ph})_3\text{Cu}]_2[\text{PF}_6]_2$ (190 mg, 0.26 mmol) and NaBArF_{24} (240 mg, 0.27 mmol) in 10 mL CH_2Cl_2 was stirred for 68 h at room temperature. Subsequently, the reaction mixture was filtered through Celite, which then was washed with CH_2Cl_2 (10 mL). All volatiles from the combined filtrates were removed under reduced pressure, which gave complex $[\text{E}^{\text{Ph}}\text{Cu}]_2[\text{BArF}_{24}]_2$ as beige solid in 81% yield (305 mg, 0.21 mmol). Complex $[\text{E}^{\text{Ph}}\text{Cu}]_2[\text{BArF}_{24}]_2$ is soluble in CH_2Cl_2 , diethyl ether, THF, dimethoxyethane and partly in CHCl_3 . Single crystals suitable for X-ray crystal structure determination were obtained by slow diffusion of n-pentane into a CH_2Cl_2 solution of $[\text{E}^{\text{Ph}}\text{Cu}]_2[\text{BArF}_{24}]_2$. Mp: 150 °C (with decomposition). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.57–7.75 (m, 54H), 8.93 (s, 6H, $\text{P}-\text{C}=\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $[\text{D}_8]\text{THF}$): δ 117.2 (br. s, $\text{Ar}-\text{C}_{\text{para}}$), 120.6 (s, $\text{Ph}-\text{C}_{\text{ortho}}$), 124.5 (q, $^1J_{\text{CF}} = 273.0$ Hz, CF_3),

129.0 (br. q, $^2J_{CF} = 31.2$ Hz, C- CF_3), 129.9 (s, Ph- C_{meta}), 130.0 (s, Ph- C_{para}), 130.4 (d, $^2J_{CP} = 26.6$ Hz, P- $C=CH$), 134.6 (s, Ar- C_{ortho}), 136.0 (s, Ph- C_{ipso}), 140.7 (d, $^1J_{CP} = 151.8$ Hz, P-C), 161.8 (q, $^1J_{CB} = 49.3$ Hz, Ar- C_{ipso}). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ -13.2. ^{19}F (235 MHz, CD_2Cl_2): δ -63.2. ^{11}B (128 MHz, CD_2Cl_2): δ -6.6 (s). IR: 1543 (w), 1373 (m), 1288 (s), 1119 (s), 775 (m), 694 (m), 567 (m). HR ESI-MS: calcd for $C_{48}H_{36}CuN_{18}O_2P_2$ (M - 2 $BArF_{24}$ - Cu): 1021.2034, found: 1021.2076.

X-ray crystal structure determination of $[E^{Ph}Cu]_2[BArF_{24}]_2$

$[C_{48}H_{36}Cu_2N_{18}O_2P_2](C_{32}H_{12}BF_{24})_2 \cdot CH_2Cl_2$, Fw = 2897.34, colourless plate, $0.33 \times 0.22 \times 0.09$ mm³, triclinic, $P\bar{1}$ (no. 2), $a = 13.6188(5)$, $b = 13.7405(6)$, $c = 36.6288(10)$ Å, $\alpha = 93.148(1)$, $\beta = 95.091(2)$, $\gamma = 119.692(1)^\circ$, $V = 5892.0(4)$ Å³, $Z = 2$, $D_x = 1.633$ g/cm³, $\mu = 0.57$ mm⁻¹. 78077 reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max} = 0.65$ Å⁻¹. Intensity data were integrated with the Eval15 software.^[39] Absorption correction and scaling was performed with SADABS^[40] based on multiple measured reflections (correction range 0.69-0.75). 27050 reflections were unique ($R_{int} = 0.028$), of which 21359 were observed [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using the program SIR-97.^[41] Least-squares refinement was performed with SHELXL-2013^[42] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. Seven of the CF_3 groups were rotationally disordered. 1891 parameters were refined with 7452 restraints (concerning distances, angles and displacement parameters of the CF_3 groups). $R1/wR2$ [$I > 2\sigma(I)$]: 0.0560 / 0.1358. $R1/wR2$ [all refl.]: 0.0734 / 0.1437. $S = 1.044$. Residual electron density between -0.88 and 1.36 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.^[43]

CCDC 965636 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.5 References

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